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(54) Title: PRODUCTION OF WATER-LESS LITHOGRAPHIC PLATES

(57) Abstract

There is described a method of preparing a water-less lithographic plate by coating a positive working photosensitive composition onto an oleophilic base imagewise exposing the plate and developing it to remove the areas of the photosensitive composition which have been light exposed, coating overall the surface of the plate with a layer of a composition which is ink-releasing or when cured becomes ink releasing, then either as a separate step or as a combined step curing the ink-releasing composition or drying the ink-releasing composition and light exposing overall the plate, then redeveloping the plate to remove the photosensitive composition remaining after the first development and any ink-releasing composition overlying the photosensitive composition.

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Production of Water-less Lithographic Plates

This invention relates to the production of so-called water-less lithographic plates.

Lithographic plates may be divided into two classes. Those which require dampening water which is fed to the non-image areas of the plate, forms a water film and acts as an ink-repellant layer; this is the so-called fount solution and those which require no fount solution are called driographs or water-less lithographic plates. Most lithographic plates at present in use are of the first type and require a fount-solution during printing. However, lithographic plates of this type suffer from a number of disadvantages. Some of these are:-

a) adjustment of the proper ink-water balance during press operation is difficult and requires great experience. If the correct ink-water balance is not achieved scumming is occasioned when the printed ink image extends into the non-image areas ruining the printed image.

b) adjustment of the ink-water balance at start-up or re-start up is particularly difficult and can not be stabilised until a large number of sheets have been printed, thus incurring waste,

c) the ink tends to become emulsified which leads to poor adherence of the ink on to the plate which causes problems in colour reproduction and in dot reproduction,

d) the printing press has to be provided with a dampening system, thus increasing its size and complexity.

e) The plate care chemistry and fount solutions require careful control and selection. Further plate cleaners contain significant levels of solvent which is not desirable.

However, with water-less plates in which the ink-releasing layer is, for example, a cured silicone layer there is no scumming and clearer images can be produced. Very often water-less plates comprise a base material, for example aluminium plate, on which a photosensitive layer is coated, on this photosensitive layer there is coated a silicone layer. After imagewise exposure and development in which selected areas of the photosensitive composition are altered, the overlying silicone layer is removed and the plate is inked up. The ink adheres only to those areas of the plate not covered by the silicone remaining after development. Thus the plate can be printed without the need to use a fount solution.

However, in practice it has proved difficult to get the silicone layer composition to adhere to the photosensitive layer. In spite of the idea of water-less plates having been described in patent specifications for at least fifteen years very little has been done to commercialise the idea and water-less plates which have been and are being sold are more expensive than the conventional plates which require a fount solution.

It is the object of the present invention to provide a novel method of preparing a water-less lithographic plate.

Therefore, according to the present invention there is provided a method of preparing a water-less lithographic plate by coating a positive working photosensitive composition onto an oleophilic base, imagewise exposing the plate and developing it to remove the areas of the photosensitive composition which have been light exposed, coating overall the surface of the plate with a layer of a composition which is ink

releasing, or when cured becomes ink releasing, then either as a separate step or as a combined step, curing the ink releasing composition or drying the ink releasing composition and light exposing overall the plate, then redeveloping the plate to remove the photosensitive composition remaining after the first development and any ink releasing composition overlying the photosensitive composition.

In order to minimise the possibility of the ink releasing substance remaining on the positive working composition after the redevelopment step an additional step between first developing step and coating overall the plate with the ink-releasing substance may be employed, which comprises treating the plate with an oleophilic coating composition which adheres to the remaining positive working composition but which does not adhere to the exposed base to form a thin optically light transparent coating on the remaining positive working composition. The ink-releasing substance does not adhere to this thin coating.

Suitable oleophilic substances to use are esters based on coconut fatty acid. Such substances are wiped on the plate after the first developing step to provide a very thin layer.

In one method of the present invention the ink-releasing composition is cured in a separate step. For example the ink-releasing composition may be heat curable.

In an alternative method of the present invention the ink-releasing composition is U.V. light curable. Thus in this method a single step only is required to cure the ink-releasing composition and to overall expose the plate.

In another method of the present invention the ink-releasing composition is initially ink-releasing but requires to be dried.

The method of the present invention yields a positive working water-less lithographic plate in which the ink releasing composition remaining on the plate constitutes the oleophobic or ink releasing areas of the plate, whilst the areas of the plate from which the photosensitive composition was removed by the second development step constitutes the oleophilic areas of the plate.

After the second development step and drying, the plate can be inked up. The ink is held in the areas between the portions of ink releasing composition which remain on the plate. No fount solution is required to differentiate between the oleophilic and the ink releasing areas of the plate when printing using an oleophilic printing ink.

The oleophilic base used in the method of the present invention is preferably an aluminium plate which will carry on its surface a thin aluminium oxide layer due to action with atmospheric oxygen. This layer may be of increased thickness due to anodising treatment of the base. Post anodic treatment of the base to increase its oleophilicity may be undertaken. This treatment following electrochemical graining provides a conventional litho base which may be used in the method of the present invention.

Alternatively the aluminium base may be an ungrained base which has been anodised and then optionally silicated. For example the following method may be used.

A solution of 3% sodium silicate was made up in deionised water. This was heated to a temperature of 50°C in a waterbath. The anodised only substrate was immersed for

30 seconds before being washed thoroughly and placed into an 80°C oven for 5 minutes.

A particularly useful base is obtained when the ungrained but anodised aluminium base is silicated as above and then coated with for example γ-aminopropyltrimethoxysilane.

A particularly useful coating solution is a 1:990 solution of γ-aminopropyltrimethoxysilane in n-heptane.

Alternatively or in addition the aluminium base may have been coated with a layer which gives the coated base improved oleophilicity over the uncoated base. Examples of such coatings are a negative working photosensitive composition or an oleophilic polymer for example ethyl cellulose or a resol type resin.

The coating over the aluminium base plate whether treated or not may be coated with a so-called primer layer as described for example in E.P. 44220, US 5061598 and E.P. 560347. Such primer layers may comprise a large variety of polymers such as polyester, polyurethanes and polyamides and help to provide a better printing surface than is afforded by uncoated aluminium.

Another base material which may be used in the method of the present invention is a plastics material base or a treated paper base as used as base in the photographic industry. A particularly useful plastics material base is polyethylene terephthalate which has been subbed to render its surface oleophilic. A so-called resin coated paper which has been corona discharge treated may also be used.

Preferably the ink releasing composition is a silicone based polymer.

Other substances which can be used instead of silicone based polymers in the ink-releasing composition include fluoro-alkyl compounds as described in USP 3910187, USP 4424325, USP 4087584 and USP 4724195.

Examples of useful silicone polymers are organo functional siloxanes. One such siloxane is available from Dow Corning as a 40% solids emulsion under the designation SYL OFF 7920.

Usefully a curing catalyst may be used in conjunction with the ink-releasing composition. For example a platinum based catalyst marketed by Dow Corning under the designation SYL OFF 7922 may be used to cure SYL OFF 7920.

A useful siloxane coating composition for use of the method of the present invention comprises :-

4 parts by weight of SYL OFF 7920
1 part by weight of SYL OFF 7922
2 parts by weight of water

This is hereinafter referred to as siloxane coating composition A.

Another useful silicone for use as release agent which is coated as an organic solvent based formulation comprises 0.375g (viscosity 500 ctsk) polydimethyl siloxane vinyl dimethyl terminated, 0.105g methylhydrodimethyl siloxane co-polymer +1 drop of platinum divinyl tetramethyl disiloxane (catalyst) in 1.53g of isopar G: toluene. (14:2.5) ratio.

Preferably the ink-releasing composition comprises a proportion of a water soluble polymer for example polyvinyl alcohol or a cellulose ether such as hydroxy propyl cellulose.

A modified siloxane composition for use in the present invention comprises :-

4 parts by weight of SYL OFF 7920

1 part by weight of SYL OFF 7922

2 parts by weight of aqueous solution which comprise 10% by weight of polyvinyl alcohol of (Gohsenol NM 14)

This siloxane composition is hereafter referred to as siloxane coating composition B.

When the ink-releasing coating composition comprises a catalyst such as SYL OFF 7922 which contains platinum the composition is heat-curable at temperatures over 100°C. Thus when such an ink-releasing coating composition is used a separate ink-releasing composition curing step is required. Examples of other platinum based catalysts are described in E.P. 560347.

Usefully the ink-releasing composition curing catalyst may be present coated on or in the oleophilic base. Thus curing of the composition takes place preferentially in those areas of the plate from which the photosensitive composition has been removed after the first developing step.

Other ink-releasing coating compositions are curable by U.V. exposure if they comprise an initiator which is activated by U.V. Such initiators are described in U.S. patent 3865588, and include aromatic ketones, hexaarylbiimidazoles and pyrilium salts.

Such initiators may also be present coated on or in the oleophilic base.

An example of a fluoro-alkyl compound composition which is U.V. curable comprises

Zonyl TM	1g
Zonyl TA-N	2g
Irgacure 907	0.1g
Methyl Ethyl Ketone	2g

This fluoro-alkyl compound composition is hereinafter referred to as fluoroalkyl coating composition C. The Zonyl products are marketed by Du Pont, the Irgacure is marketed by Ciba-Geigy.

An example of a fluoro compound composition which is initially ink-releasing but in use requires to be air dried at about 100°C is a 17% by weight of ZONYL 8070 dispersed in water. ZONYL is a fluoro alkyl polymer marketed by Du Pont.

This is hereinafter referred to as fluoroalkyl coating composition D.

Usefully a curing inhibitor may be present in the positive layer. This reduces the amount of ink-releasing composition which adheres to the positive photosensitive composition areas which are left after the first development and exposure. This aids in the complete removal of such positive areas after the second exposure and development. An example of a suitable curing inhibitor is hydroquinone.

In order to reduce the amount of ink releasing composition which sticks to the positive photosensitive composition left after the first development the binder for this

photosensitive composition may comprise at least one cellulosic compound such as ethyl cellulose.

Depending on the optical sensitivity of the photosensitive composition the imagewise exposure may be a contact exposure, a projection exposure or an exposure in an image setter to an electromagnetic radiation or heat source, typically a scanning laser.

Preferably the positive working photosensitive composition comprises an 0-quinone diazide compound.

Examples of particularly preferred o-quinone diazide compounds are disclosed in a variety of publications such as U.S. Pat. Nos. 2,766,118; 2,767,092; 2,772,972; 2,859,112; 2,907,665; 3,046,110; 3,046,111; 3,046,115; 3,046,118; 3,046,119; 3,046,120; 3,046,121; 3,046,122; 3,046,123; 3,061,430; 3,102,809; 3,106,465; 3,635,709 and 3,647,443 and these compounds may preferably be used in the invention. Among these, particularly preferred are o-naphthoquinonediazidosulfonates or o-naphthoquinonediazidocarboxylates of aromatic hydroxyl compounds; o-naphthoquinonediazidosulfonic acid amides or o-naphthoquinonediazido- carboxylic acid amides of aromatic amine compounds, for instance, esters of benzoquinone-1, 2-diazidosulfonic acid or naphthoquinone-1, 2-diazidosulfonic acid with polyhydroxyphenyl (hereinafter the term "ester" also include partial esters); esters of naphthoquinone-1, 2-diazido-4-sulfonic acid or naphthoquinone-1,2-diazido-5-sulfonic acid with pyrogallol/acetone resins; esters of benzoquinone-1, 2-diazidosulfonic acid or naphthoquinone-1,2-diazidosulfonic acid with novolak type phenol/formaldehyde resins or novalak type cresol/ formaldehyde resins; amides of poly(p-aminostyrene) and naphthoquinone-1, 2-diazido-4-sulfonic acid or naphthoquinone-1,2-diazido-5-sulfonic acid; esters of poly(p-hydroxystyrene) and naphthoquinone-1,2- diazido-5-sulfonic acid; esters of polyethylene glycol with

naphthoquinone-1,2-diazido-4-sulfonic acid or naphthoquinone-1, 2-diazido 5-sulfonic acid: amides of polymeric amines with naphthoquinone-1,2-diazido-4-sulfonic.

A particularly useful positive working composition comprises a triarylmethane dye, a triazine acid generator, 2,4 Naphthaquinone diazide sulphonic acid ester of a phenol resin.

This is hereinafter referred to as positive working photosensitive composition A.

An example of a developing solution used in both the first development step and second development step in the process of the present invention that is to say to remove the exposed positive photosensitive areas of the photosensitive composition after the first exposure are and after the second exposure is an aqueous solution of 8% metasilicate, 0.1% of an organic phosphite ester of an ethoxylated alcohol and 0.01% of polyoxy propylene methyl ethyl ammonium chloride. This is hereinafter referred to as Developing solution A.

In order to illustrate the various steps of the process of the present invention reference is made to the accompanying drawings.

Figures I, II, III, IV and V show the steps in the preparation of a water-less lithographic plate from a presensitised lithographic plate.

In figure I the starting plate comprises the positive working photosensitive composition A on an aluminium plate.

In figure IA there is coated on the grained oleophilic aluminium plate 1 the positive working photosensitive composition 2. Shown above the plate is a mask 3.

This plate is treated by the following steps, exposure through the mask 3, then developed in developing solution A. This development step removes the light exposed areas of the photosensitive composition 2. The developed plate is then coated overall with siloxane coating composition A.

The siloxane coating is then heat cured at 110°C for one minute.

This yields the plate as shown in figure IB, wherein 1 is the aluminium plate, 2 shows the photosensitive composition remaining after development and 5 shows the cured siloxane both on the remaining photosensitive composition 2 and directly coated on the plate 5a. The plate shown in IB is then subjected to an overall visible light exposure and is then redeveloped in developing solution A. The resulting plate is as shown in figure IC.

The grained oleophilic aluminium plate 1 has areas of 1b with no coating thereon. On areas 1c it is coated with the cured siloxane coating 5.

The plate shown in figure IC can be inked up with an oleophilic ink which adheres to areas 1b of the aluminium plate but not to areas 1c which is coated with the cured siloxane 5. This inked up plate can be used as a water-less printing plate requiring no fount solution.

In a small modification to the method described with reference to the plate of figure I. After the first development step the plate 1 was coated overall with silicone coated composition B which comprises a small proportion of polyvinyl alcohol. This

has the effect of making it easier to remove the siloxane coating 5 on the remaining photosensitive composition 2 in figure B but the siloxane in figure IC was not affected.

In figure II the plate comprising the same aluminium plate as used in figure I was coated with the same positive working coating composition 2 as used in figure I.

The plate of figure IIA was then exposed through mask 3, developed in developing solution A to remove the light exposed areas of the photosensitive composition 2. The developed plate was then coated overall with the fluoro coating composition C which is U.V. light curable.

The plate was overall U.V. light exposed. This cures the fluoro coating composition and exposes the remaining photosensitive composition. The plate was then redeveloped in developing solution A. The resulting plate is as shown in figure IIC. The grained oleophilic aluminium plate has areas 1b with no coating thereon. On areas 1c it is coated with the U.V. light cured fluoro coating 5.

The plate shown in figure IIC can be inked up with an oleophilic ink which adheres to areas 1b of the aluminium plate but not to areas 1c which is coated with the cured fluoro composition 5. This inked up plate can be used as a water-less printing plate requiring no fount solution.

In figure III the plate comprising the same aluminium plate as used in figure I was coated with the same positive working coating composition 2 as used in figure I.

The plate of figure III was then exposed through mask 3 and then developed in developing solution A to remove the light exposed areas of the photosensitive composition 2 as shown in Fig IIIB.

The developed plate was then coated overall with a Coconut fatty acid. This remained as a very thin layer 7 on the remaining photosensitive composition 2 but did not adhere to the uncovered plate 6 as shown in Fig III C.

This plate was then coated overall with the fluoro-alkyl coating composition D shown as 5 and air dried at 120°C for one minute as shown in Fig III D. The plate was then subjected to overall light exposure and was re-developed in developing solution A. The resulting plate is as shown in IIIE. The grained aluminium plate 1 has areas 1b with no coating thereon and areas coated with the ink-releasing fluoro-alkyl coating 5.

The plate shown in figure IIIE can be inked up with an oleophilic ink which adheres to areas 1b of the aluminium plate but not on areas which are coated with the cured fluoro-alkyl 5. This inked up plate can be used as a water-less printing plate requiring no fount solution.

In figure IV the plate comprising the same aluminium plate as used in figure I coated on this plate is a negative working coating composition 9 which comprised a triarylmethane dye, a condensation product of 4-diazodiphenylamine sulphate and formaldehyde (p-toluene sulphonic acid salt) and an epoxide resin.

Coated on the diazo resin 9 is the same positive working photosensitive composition A as used in figure I this is shown as 2. These coatings are shown in figure IVA.

The plate of figure IVA is then exposed through mask 3, to expose only the overlying positive coating, developed in developing solution A, thus the exposed areas of the positive photosensitive layer 2 are removed by the development step and overall coated with siloxane coating composition A shown as 5. The siloxane coating is then heat cured at 110°C for 1 minute.

The plate of IVB is then overall light exposed and is redeveloped in developing solution A. This yields the plate shown in figure IVC. In this figure the plate 1 is coated overall with hardened diazo resin 9c. On the areas of the plate of figure IVC which were exposed in the first exposure step through the mask 3 is the cured siloxane resin 5. The areas of the plate not covered by the siloxane resin 5 comprise the photohardened diazo resin which is especially oleophilic. Thus the plate of figure IVC can be inked up and the oleophilic ink adheres extremely well to the areas 9c not covered with the siloxane and can be used as a water-less lithographic plate.

In figure V again the same aluminium plate is used. On this plate is coated a layer 12 of ethyl cellulose. This substance when dried forms an oleophilic layer. Coated on the ethyl cellulose layer 12 is a layer of positive working photosensitive resin. These coatings are shown in figure VA.

The plate in figure VA is then exposed through mask 3, developed in developing solution A and overall coated ink siloxane coating composition A shown as 5 in figure VB. The siloxane coating is then heat cured at 110°C for 1 minute.

The plate of figure VB is then overall light exposed and is redeveloped in developing solution A. This yields the plate shown in VC. This plate can then be inked-up with a oleophic ink which adheres only to the ethyl cellulose layer 12. The ink does not

adhere to the areas of ethyl cellulose coated by the silicone coating 5. Thus a water-less printing plate is produced.

Other oleophilic yielding layers can be used in the plate of figure VA instead of ethyl cellulose.

After the redevelopment step all the plates prepared with reference to figures I to V were dried and were then inked using a rubber roller and water-less plate ink. They were then placed in a printing press and in every case several thousand good prints were obtained.

Claims:-

1. A method of preparing a water-less lithographic plate by coating a positive working photosensitive composition onto an oleophilic base, imagewise exposing the plate and developing it to remove the areas of the photosensitive composition which have been light exposed, coating overall the surface of the plate with a layer of a composition which is ink-releasing or when cured becomes ink releasing, then either as a separate step or as a combined step curing the ink-releasing composition or drying the ink-releasing composition and light exposing overall the plate, then redeveloping the plate to remove the photosensitive composition remaining after the first development and any ink-releasing composition overlying the photosensitive composition.

2. A method according to claim 1 which comprises the additional step between the developing step and the step of coating overall the plate with an ink releasing substance of treating the plate with an oleophilic coating composition which adheres to the remaining positive working composition but which does not adhere to the exposed base to form a thin optically light transparent coating on the remaining positive working composition.

3. A method according to claim 2 wherein the oleophilic coating composition comprises an ester based on coconut fatty acid.

4. A method according to claim 1 wherein the ink-releasing composition is heat curable.

5. A method according to claim 1 wherein the ink-releasing composition is UV curable.

6. A method according to claim 5 wherein a single exposure to UV light exposes the photosensitive composition and cures the ink-releasing composition.

7. A method according to claim 1 wherein the ink-releasing composition is initially ink-releasing but requires to be dried.

8. A method according to claim 1 wherein the oleophilic base is an aluminium plate which has been physically or chemically treated to render it oleophilic.

9. A method according to claim 1 wherein the ink-releasing composition is either a silicone based polymer or a fluoroalkyl compound.

10. A method according to claim 1 wherein the ink-releasing composition comprises a proportion of a water-soluble polymer.

11. A method according to claim 10 wherein the water-soluble polymer is polyvinyl alcohol or hydroxypropyl cellulose.

12. A method according to claim 1 wherein positive working photosensitive composition comprises an 0-quinone diazide compound.

13. A method according to claim 1 wherein there is present between the base plate and the positive working photosensitive composition an oleophilic layer to which the positive working photosensitive composition can adhere.

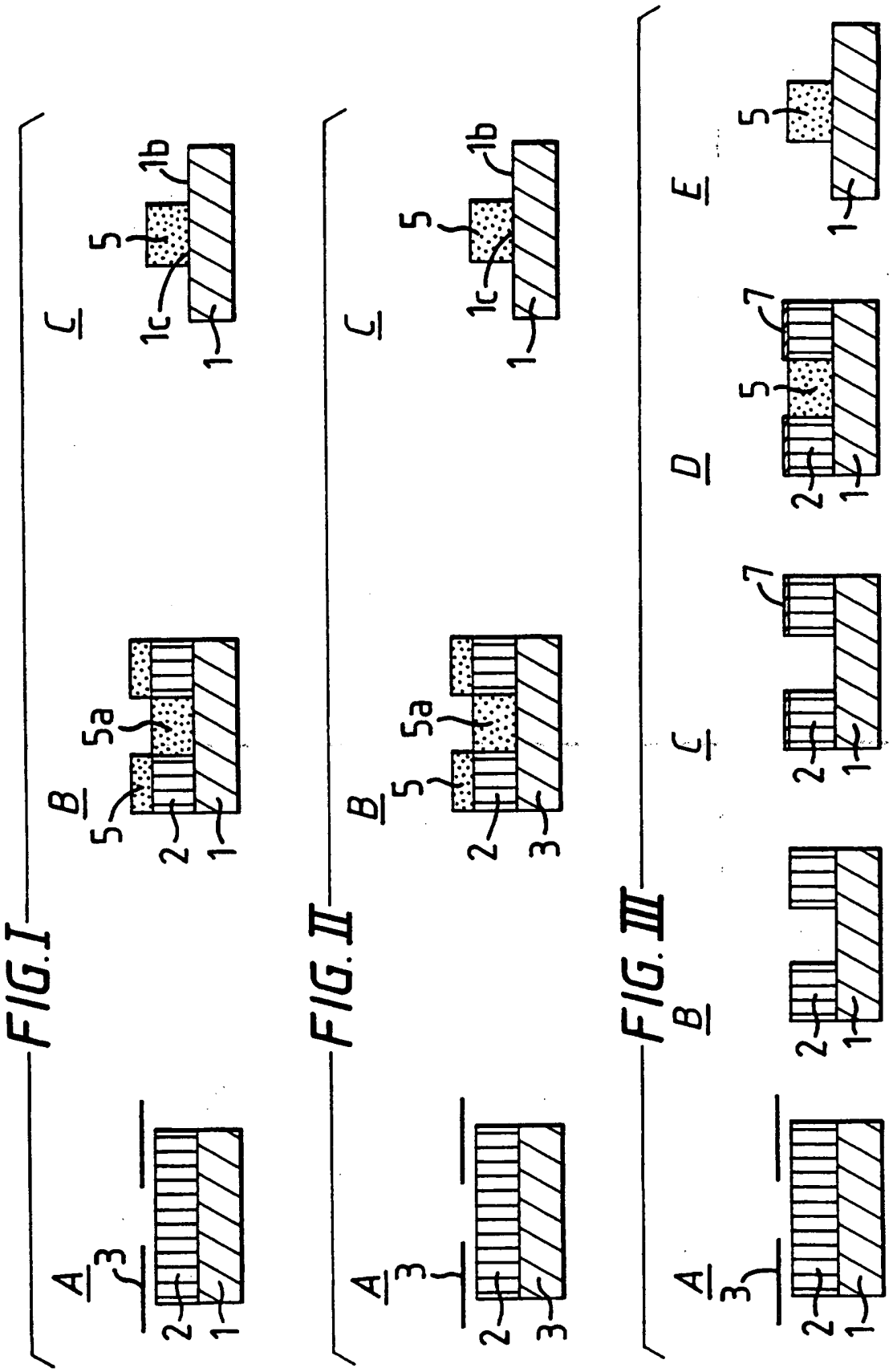
14. A method according to claim 13 wherein the oleophilic layer is a negative working plate.

15. A method according to claim 13 wherein the oleophilic layer is a layer of ethyl cellulose.

16. A method according to claim 1 wherein a curing inhibitor for the ink-releasing composition is present in the positive working photosensitive layer.

17. A method according to claim 16 wherein the curing inhibitor is hydroquinone.

18. A method according to claim 1 wherein the positive working photosensitive composition comprises at least one cellulosic compound.



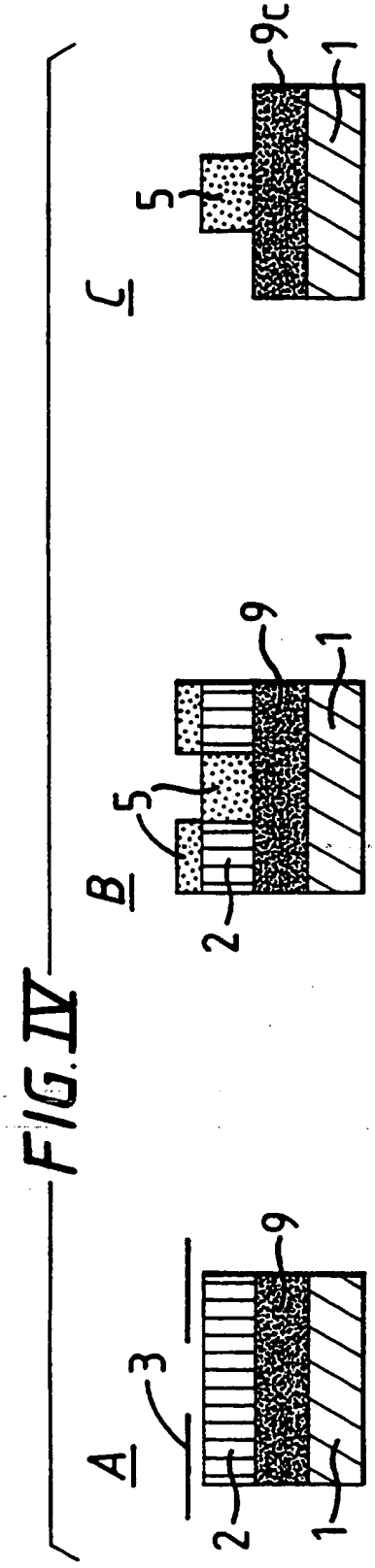


FIG. IV

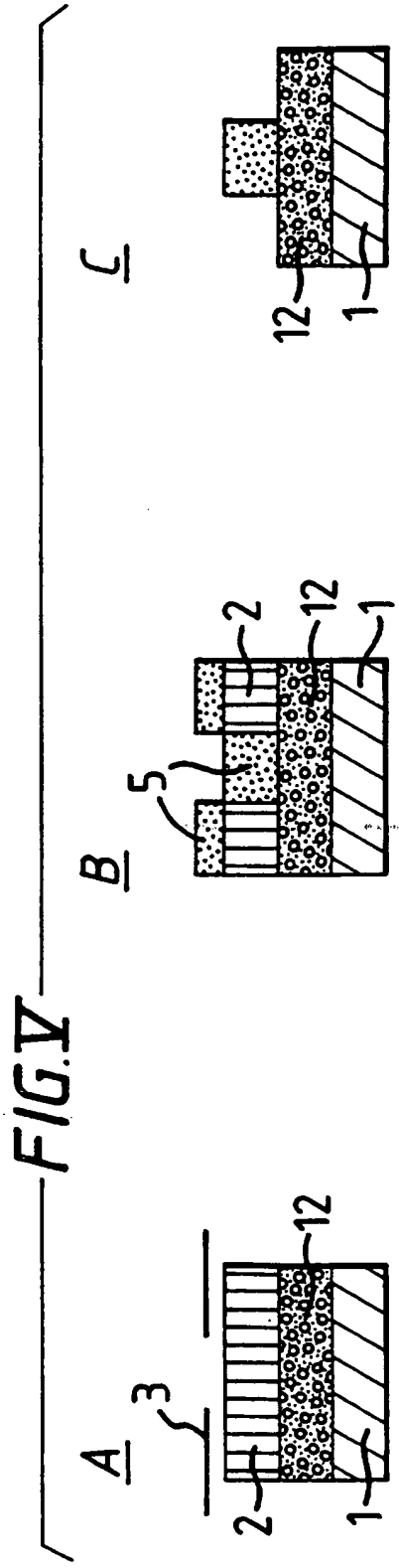


FIG. V

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/GB 95/02782

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/075 G03F7/20 G03F7/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DD,A,157 125 (E. HERMANIES) 13 October 1982 see the whole document ---	1,4-9, 12,13, 16-18
Y	DD,A,200 108 (H. BLANKENSTEIN) 16 March 1983 see the whole document ---	1,4-9, 12,13, 16-18
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 19, no. 10, March 1977 NEW YORK, US, page 4014 ANONYMOUS 'Lift Off Technique. March 1977.' see the whole document --- -/--	1,4-9, 12,13, 16-18

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Intern. nal Application No
PCT/GB 95/02782

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 241 486 (P.W. GREUBEL) 22 March 1966 ---	
A	DE,A,37 12 335 (VDO SCHINDLING) 20 October 1988 ---	
A	PATENT ABSTRACTS OF JAPAN vol. 007 no. 093 (P-192) ,19 April 1983 & JP,A,58 018634 (DAINIPPON INSATSU KK) 3 February 1983, see abstract ---	
A	D.J. ELLIOTT 'Integrated Circuit Fabrication' 1982 , MCGRAW-HILL , NEW YORK, US see page 27 - page 29 -----	

1

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Information on patent family members

Inter. al Application No
PCT/GB 95/02782

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DD-A-157125		NONE	
DD-A-200108		NONE	
US-A-3241486	22-03-66	NONE	
DE-A-3712335	20-10-88	DE-D- 3750162	04-08-94
		EP-A- 0290670	17-11-88
		JP-A- 63282735	18-11-88